# Residues from Coal Conversion and Utilization: Advanced Mineralogical Characterization and Disposed By-product Diagenesis

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Class C fly ash, some flue gas desulfurization (FGD) residues, and by-products of many clean coal technologies are cementitious and subject to chemical and mineralogical changes when utilized or disposed. The established tests of chemical and physical properties, which often yield results encouraging for high-volume utilization, may not be representative of the long-term behavior of these materials when exposed to the environment. Recent studies in our group have shown that certain cementitious Coal Combustion Byproducts (CCBs) that have been landfilled in the natural environment, undergo mineralogical alteration in processes analogous to natural *diagenesis*. This diagenesis is typically accompanied by a much lower strength and greatly increased permeability. The altered CCBs ultimately obtain structural properties more similar to soils than to concrete, which means that long-term models of environmental behavior based on short-term tests may not be dealing with the appropriate material. However, we do not know whether these results are representative of all CCB materials utilized or disposed in the natural environment.

Attempts to understand long-term processes involved in these complex, inhomogeneous, non-equilibrium systems require quantitative mineralogical characterization by X-ray diffraction (QXRD). CCB materials typically contain a large number of crystalline phases, with many present in only small quantities. Many of these phases exhibit solid solution behavior and polymorphism, as well as varying degrees of crystalline order. Additionally, a significant amorphous or glassy content is typically present. These factors make conventional QXRD analysis unusable or unreliable. Whole-pattern methods such as Rietveld analysis can overcome many of the limitations of conventional QXRD, but have not been developed and evaluated for materials as complex as CCBs.

The goals of this research are to: (1) apply the whole-pattern Rietveld quantitative X-ray diffraction (QXRD) method to chemically and mineralogically complex coal combustion by-products (CCB), and critically evaluate the factors affecting the quality of the analytical results, (2) use Rietveld QXRD to determine the mineralogy of landfilled or utilized CCB materials, and (3) combine these results with previous studies to elucidate further the nature and importance of CCB diagenesis. The following sections describe progress during the past year.

The Rietveld Method uses the whole diffraction pattern to model the parameters that control peak position, peak intensity and peak and background shape: (1) Bragg diffraction position and intensity which are a function of crystal structure and chemical composition, (2) sample (e.g., level of crystalline order) and specimen (e.g., preferred orientation) effects; and (3) instrumental effects. The modeled diffraction profile is least squares fit to the experimental diffraction profile. A public domain Rietveld code called GSAS (General Structure Analysis System), which is maintained by personnel at DOE's LANL, is being utilized in this research.

The crystal structure input needed to perform Rietveld analysis on CCB materials has been obtained from the literature, checked for errors, critically evaluated for applicability to the GSAS Rietveld code, and posted to our website [**http://qxrd.chem.ndsu.nodak.edu/ccbs/**] for use by the materials analysis community.

Once structure data are available, to many analysts doing Rietveld QXRD might seem straightforward: (1) obtain a diffraction pattern over a large scan range, (2) fix or refine some sample and specimen parameters, (3) find the best least squares fit of experimental and calculated XRD profile by trial-and-error, and (4) obtain quantitative phase analysis results from the crystalline phase scale factors, using an internal standard to account for amorphous phases. Because CCBs are such complex assemblages they often have hundreds of parameters to be refined, and many of those parameters are correlated. This increases the probability of obtaining false minima and incorrect results. The situation is improved if some parameters can be predetermined and fixed.

We have performed sensitivity analyses on most of the variables that will affect Rietveld QXRD success (i.e., will the refinement converge) and accuracy with complex CCB assemblages. We use standard mixtures of NIST SRMs and stable laboratory reagents such as alpha- and gamma- $Fe_2O_3$, and $CaCO_3$. Based on recoveries of weight percentages of standard mixtures, the following issues and factors have been studied: (1) selection of data acquisition parameters that result in a satisfactorily accurate result at the minimum cost in instrument time, (2) effects on accuracy from the choice of an internal standard, (3) value of fixing the profile model based on predetermined instrumental parameters, (4) influence of the choice of structure data, especially thermal parameters, on accuracy, (5) modeling preferred orientation, (6) dealing with compositional variability (solid solution) from sample to sample, (7) accuracy of determinations of amorphous content and its effect on error propagation, (8) effect of severe overlap on success and accuracy, and (9) correcting for unmodeled (by GSAS) microabsorption effects. The object is to give occasional users Rietveld QXRD protocols with an estimate of the accuracy and level of error that can be expected when following a particular protocol. Table 1 give sample results for a standard mixture of five crystalline phases plus a rutile internal standard.

Table 1. Refined weight percentages for a five phase mixture of reference materials (rutile as the internal standard)

| Phase | Reference Weight Percents | Rietveld QXRD | Relative Error |
|---|---|---|---|
| Quartz | 28.6 | 29.2 | 2.0% |
| Hematite | 30.1 | 31.5 | 4.5% |
| Calcite | 23.4 | 22.1 | 5.9% |
| Periclase | 9.7 | 10.5 | 8.3% |
| Silicon | 5.0 | 5.3 | 4.8% |

Qualitative XRD is underway for core from two CCB landfills and a utilization sites: (1) FGD from a Midwest utility burning Montana coal, up to 5 years exposure, (2) Class F fly ash from an electric power-generating utility in Kentucky [cooperative work with a consortium of entities headed by the USGS]; up to 10 years exposure, and (3) CFBC/stoker ash mixture from a road embankment in Indiana; up to 3 years exposure. Materials from two other sites are scheduled for collection and analysis this summer. Powder patterns are being archived for Rietveld QXRD analyses later this year. Due to the flood in Grand Forks, a *ca.* one year delay has been experienced by the UND EERC in obtaining electron microprobe data needed for these analyses.

**Publications**

McCarthy, G.J., Butler, R.D., Grier, D.G., Adamek, S.D., Parks, J.A., and Foster, H.J., "Long-Term Stability of Disposed Coal Combustion Byproducts," *Fuel*. 76, 697-703 (1997).

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**Presentations**

Winburn, R.S., Grier, D.G. and McCarthy, G.J., "Quantitative XRD Analysis of Coal Combustion By-products by the Rietveld Method," 1997 Denver Conference on Applications of X-Ray Analysis, Steamboat Springs, CO, August, 1997.

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